

# UTILIZATION OF WASTE

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## PRODUCTION OF GLASS CERAMICS AS A METHOD FOR COMPREHENSIVE UTILIZATION OF CHEMICAL INDUSTRY WASTE

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A variant of comprehensive utilization of waste generated at a chemical enterprise in the production of pyroxene glass ceramics is considered. The structure and properties of synthesized glass ceramic materials are investigated.

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The production of glass ceramic materials based on mineral waste generated by different industries is a promising line. Whereas in 1960–1980s the main research related to this issue was concentrated in research and development centers of the Soviet Union [1–3], in recent years the amount of publications by foreign researchers has significantly grown [4–6].

The use of inorganic industrial waste as raw materials solves two problems simultaneously: it addresses the increasing shortage of raw materials for the glass industry and provides for economically effective utilization of waste. The main technical problems in developing production of glass ceramics based on such waste are the impossibility to control the chemical composition of the glass batch components and the inconvenience of transporting mineral waste from the site of their origin to the site of their use.

Consequently, it is advisable to develop mixture compositions that can make use of various inorganic kinds of waste generated by a single large industrial enterprise. The batch composition should allow for variations in the chemical composition of source materials without perceptible modifications of the melting and crystallization properties of resulting glasses and consumer properties of articles produced from such glass ceramics. Accordingly, the most promising are glasses with the following content (here and elsewhere wt.%): 35–60 SiO<sub>2</sub>, 2–15 Al<sub>2</sub>O<sub>3</sub>, 1–26 (FeO + Fe<sub>2</sub>O<sub>3</sub>), 9–25 CaO, 1–20 MgO, 0–10 R<sub>2</sub>O, as well as impurities of P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, ZnO, ZrO<sub>2</sub> and other oxides), since they have a relatively low melting temperature and in crystallizing form pyroxene glass ceramics despite significant fluctuations in their chemical composition [2].

The present study is dedicated to developing a method for preparing batch for pyroxene glass ceramics based on inorganic waste of a large chemical enterprise producing combined mineral fertilizers, namely, the Meleuzovskii Chemical Works (Bashkortostan). This enterprise produces sulfuric acid, sodium silicofluoride, ammonium, ammophos, and other chemicals, which involves generating large quantities of inorganic waste, of which the main are phosphogypsum and pyrite cinders, which form large dumps. At the same time, substantial quantities of other waste products are formed, in particular, waste vanadium catalyst, dolomite dust, and substandard products, which can be used as batch components in producing glass ceramics of the pyroxene composition. The main purpose of our study is to search for the optimum combinations of the above mentioned wastes with small additives of traditional components of the glass industry, which are involved in the main production cycles at the enterprise.

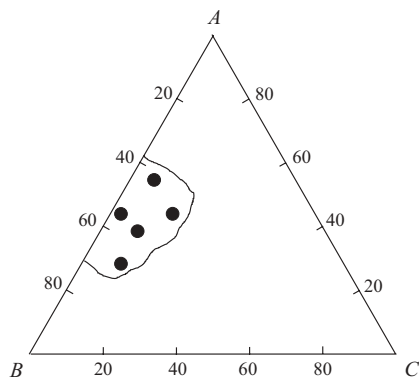
The chemical compositions of the raw materials are listed in Table 1. The main batch components for pyroxene glass ceramics based on the specified waste are: sources of SiO<sub>2</sub> (sand and waste vanadium catalyst); sources of CaO (phosphogypsum and dolomite); a source of Fe<sub>x</sub>O<sub>y</sub> (pyrite cinders). The crystallization catalysts in such mixture can be V<sub>2</sub>O<sub>5</sub> and P<sub>2</sub>O<sub>5</sub>. Furthermore, the high content of iron oxides should have a favorable effect on the crystallization process.

Additives of substandard Na<sub>2</sub>SiF<sub>6</sub> facilitate the introduction of sodium oxide (a flux) and fluorine (a crystallization catalyst). Moreover, according to the earlier research data [2], it is advisable to introduce up to 10% of Al<sub>2</sub>O<sub>3</sub> into the batch. This can be accomplished by adding alumina.

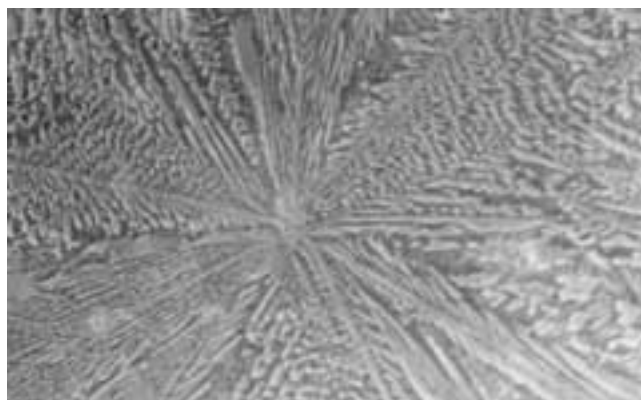
Preliminary experiments indicated that the required melting (melting temperature of 1400°C) and crystallization

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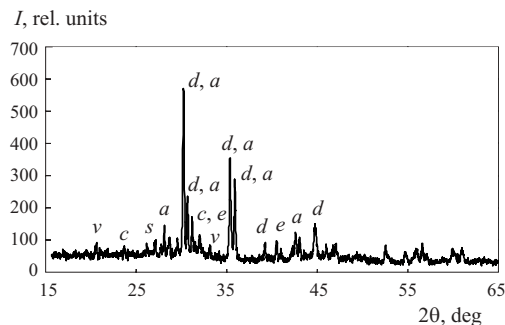
**Fig. 1.** Range of formation of pyroxene glass ceramics (●) with different component ratios: *A*) phosphogypsum + dolomite (4%); *B*) waste vanadium catalyst + sand (5%) + alumina (2%), *C*) pyrite cinders.



**Fig. 2.** Structure of glass ceramic based on waste generated in production of combined mineral fertilizers.

properties of glass can be ensured by introducing 7–18% additional batch components into the basic mixture that includes inorganic wastes of the main production processes.

To identify the range of formation of pyroxene glass ceramics, glasses were melted and crystallized with different ratios of three main groups of waste and a constant quantity



**Fig. 3.** Typical diffraction pattern of glass-ceramic material: *d*) diopside, *a*) augite, *c*) clinoenstatite; *e*) enstatite, *s*) sanidine, *v*)  $\text{NaV}_6\text{O}_{11}$ .

of batch additives (%): 5 sand, 10 substandard  $\text{Na}_2\text{SiF}_6$ , 4 dolomite, and 2 alumina.

Glasses were melted in alundum crucibles at 1380°C for 1 h. Glass samples were cast in stainless-steel molds and subjected to one-stage crystallization regime in a muffle furnace, which is the optimum regime for glasses of this composition [7]: 1.5 h at 870°C.

As a consequence, batch compositions were identified that provided for the production of glasses which in crystallizing form pyroxene glass ceramics (Fig. 1). A typical view of the resulting crystalline structure is shown in Fig. 2. The phase composition of glass ceramic materials inside the crystallization field (Fig. 1) is represented by diopside  $(\text{Ca, Mg})(\text{SiO}_3)_2$  and diopside-hedenbergite solid solutions with impurities of augite  $(\text{Ca, Mg, Fe, Al})(\text{Si, Al})_2\text{O}_6$ , clinoenstatite  $\text{MgSiO}_3$ , enstatite  $(\text{Mg, Fe})\text{SiO}_3$  and sanidine  $(\text{K, Na})(\text{Si}_3\text{Al})\text{O}_8$  (Fig. 3). The primary crystalline phases identified as related to the presence of  $\text{V}_2\text{O}_5$  and F in the used waste are  $\text{NaV}_6\text{O}_{11}$  and  $\text{CaF}_2$ .

Additional experiments indicated that the additive of substandard  $\text{Na}_2\text{SiF}_6$  may vary within the limits of 5–15% without changing the phase composition of glass ceramics, and the sand additive may vary within the limits of 5–20%, provided that the deficit of  $\text{SiO}_2$  is compensated by modifying the share of the waste vanadium catalyst. A sufficiently large formation range of pyroxene glass ceramics (Fig. 1)

**TABLE 1**

Batch components*	Weight content, %							
	$\text{SiO}_2$	$\text{CaO}$	$\text{MgO}$	$\text{Al}_2\text{O}_3$	$\text{R}_2\text{O}$	$\text{Fe}_x\text{O}_y$	$\text{SO}_3$	F
Phosphogypsum**	0.8	30.0	—	0.1	0.2	0.1	43.0	0.5
Pyrite cinders	12.5	1.2	0.4	1.5	—	48.0	2.2	—
Substandard $\text{Na}_2\text{SiF}_6$	32.0	—	—	—	33.0	—	—	35.0
Waste vanadium catalyst***	82.0	—	—	—	5.4	—	4.6	—
Dolomite dust	3.0	27.0	13.8	1.6	—	0.2	—	—
Sand	98.9	0.5	—	0.5	—	0.1	—	—

\*  $\text{Al}_2\text{O}_3$  content is 10.0%.

\*\* Including 1.8%  $\text{P}_2\text{O}_5$ .

\*\*\* Including 6.0%  $\text{V}_2\text{O}_5$ .

guarantees that variations in the composition of industrial waste used in the batch preparation will not modify the structure and properties of the obtained glass ceramics. Furthermore, this approach to batch preparation makes it possible to adjust the batch composition depending on the current purposes of utilization of specific waste.

For instance, the problem of utilization of waste vanadium catalysts arises periodically when the catalysts are replaced. In this case their content in the batch can be increased by modifying the quantity of sand. However, the batch composition in this case should remain within the limits of the range of formation of pyroxene glass ceramics according to the diagram (Fig. 1). On the other hand, not every producer of fertilizers can implement purification of gases emitted in glass melting involving sulfur oxides that result from disintegration of phosphogypsum. In this case phosphogypsum can be fully or partly replaced by dolomite or lime with a minimum correction of the total content of the batch components. Examples of such corrections of the batch composition are given in Table 2 and 3. The chemical and the phase composition of synthesized glass ceramics, as well as their properties, are very similar (Table 4).

The proposed approach to batch preparation for production of glass ceramics based on comprehensive utilization of industrial waste generated in production of mineral fertilizers makes it possible to vary the composition of batch materials depending on excess or shortage of certain kinds of waste, without modifying the composition and properties of the end product. Accidental fluctuations in the chemical composition are not significant either, as they have no effect on the melting properties of glass and the phase composition of glass ceramics.

## REFERENCES

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TABLE 2

Batch mixture	Weight content, %						
	phosphogypsum	waste vanadium catalysts	pyrite cinders	alumina	sand	substandard Na <sub>2</sub> SiF <sub>6</sub>	dolomite dust
1	38.5	25.8	14.2	1.9	5.8	9.7	4.1
2	24.7	14.2	8.6	2.2	15.7	12.8	21.8

TABLE 3

Glass-ceramic	Weight content, %										
	SiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>x</sub> O <sub>y</sub>	P <sub>2</sub> O <sub>5</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	F	SO <sub>3</sub>
1	37.2	1.5	5.3	18.2	2.3	25.0	1.9	3.7	1.7	2.9	0.3
2	40.8	0.9	5.9	14.4	1.1	23.2	5.2	2.5	0.9	4.9	0.2

TABLE 4

Parameter	Glass-ceramic	
	1	2
Density, g/cm <sup>3</sup>	3.5 ± 0.1	3.1 ± 0.1
Microhardness, GPa	7.22 ± 0.07	7.35 ± 0.07
Compression strength, MPa	112 ± 25	118 ± 20
TCLE, 10 <sup>-7</sup> K <sup>-1</sup>	95.3 ± 1.8	93.2 ± 2.2
Heat resistance, °C	310	290

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